Journal of Alloys and Compounds 689 (2016) 489–499

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Microwave synthesis of nitrogen-doped mesoporous carbon/nickel-cobalt hydroxide microspheres for high-performance supercapacitors

Juan Xu [a], Zhengwei Ju [a], Jianyu Cao [a, **], Wenchang Wang [a], Cheng Wang [a], Zhidong Chen [a, b, *]

[a] School of Petrochemical Engineering, Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China
[b] Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Jiangsu Key Laboratory of Materials Surface Science and Technology, School of Materials Science and Engineering, Changzhou 213164, China

ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form
12 July 2016
Accepted 1 August 2016
Available online 3 August 2016

Keywords:
Nickel-cobalt layered double hydroxide
Nitrogen-doped mesoporous carbon
Microwave method
Asymmetric supercapacitor

ABSTRACT

A novel microsphere-like nitrogen-doped mesoporous carbon/nickel-cobalt layered double hydroxide (NMC/NiCo-LDHs-M) composites were successfully synthesized for the first time via a facile and cost-effective microwave method. The NMC/NiCo-LDHs-M electrode displays outstanding pseudocapacitance performances, including a high specific capacitance (2498 F g^{-1} at 1 A g^{-1}), excellent rate capability and good charge-discharge stability, owing to the large surface area, appropriate pore size, rich mesoporous volume, low reaction resistance and high nitrogen amount. Moreover, an asymmetric supercapacitor using NMC/NiCo-LDHs-M as positive materials and NMC as negative materials was assembled to further investigate the electrochemical performances of NMC/NiCo-LDHs-M, which exhibited a high specific capacitance of 272.6 F g^{-1} at 1 A g^{-1} and outstanding electrochemical capacitance retention of 87.2% of initial capacitance after 10,000 cycles. These results indicated that the NMC/NiCo-LDHs-M microspheres were promising materials for high-performance supercapacitors and the microwave method was a potential approach for the design and preparation of diverse supercapacitor materials.

1. Introduction

The worsening energy crises and environmental issues have stirred up the urgent demand of efficient energy storage and conversion devices with high energy and power densities. Supercapacitors, as promising energy storage devices, have attracted considerable attention for providing higher power density than batteries, higher energy density than conventional electrostatic capacitors. Based on their charge storage mechanisms [1], supercapacitors can be generally classified into two categories: double-layer capacitors (EDLCs) and electrochemical pseudocapacitors (EPCs) [2]. Particularly, the specific capacitance value of EPCs is almost 10–100 times that of EDLCs.

The electrochemical performances of EPCs were primarily determined by the physical and chemical characteristics of their electrode materials. Among the pseudocapacitive active species, double hydroxides were considered as promising electrode materials due to their high capacitance, fast redox activities, low cost and environmentally friendly nature [3]. In particular, nickel cobalt layered double hydroxides (NiCo-LDHs) have been widely studied as high-performance electrode materials for EPCs due to their abilities to offer rich redox reactions with excellent electrochemical activity and electrical conductivity [4–8]. However, the pristine NiCo-LDHs often suffer from poor cycle stability and great capacitance loss due to the slow mass diffusion and electron transfer rate [9]. Some efforts have been made to improve the pseudocapacitive performance of NiCo-LDHs by creating special nanostructures and introducing conductive nanoporous carbon [10,11]. For example, a hierarchical graphene/$Ni_{0.6}Co_{0.4}(OH)_2$ composite was prepared via a facile one-pot solvothermal method, which attained a maximum specific capacitance of 1911 F g^{-1} at 2 A g^{-1} and a high capacitance

* Corresponding author. School of Petrochemical Engineering, Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China.
** Corresponding author. School of Petrochemical Engineering, Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China.
E-mail addresses: jyucao@hotmail.com (J. Cao), cjytion@163.com (Z. Chen).

http://dx.doi.org/10.1016/j.jallcom.2016.08.006
0925-8388/

retention of about 74% even after 1000 cycles at a high current density of 20 A g^{-1} [12]. Warsi et al. successfully synthesized $Ni_{0.33}Co_{0.67}(OH)_2$ nanoflakes coated carbon fibers using ammonia as alkali source, which exhibited an optimum specific capacitance of 1809 F g^{-1} at a current density of 1 A g^{-1} and only 4.6% loss after 3000 cycles [13]. For the $NiCo(OH)_2$ film grown on CNTs, the composite is stable with capacitance retention of more than 80% after 5000 cycles [14]. Li et al. reported that the CNTs/$NiCo(OH)_2$ nanoflakes composites delivered a specific capacitance of 1843 F g^{-1} at 1 A g^{-1} [15]. Cheng et al. also designed a CNTs/NiCo-LDHs core-shell nanostructure and found this novel compound exhibited a substantially improved capacitance retention rate [16]. Flower-like graphene/NiCo-LDHs composites were prepared by a microwave heating reflux method and a high specific capacitance of 1980 F g^{-1} [17]. In spite of these remarkable progresses, the specific capacitance and cycle performances of C/NiCo-LDHs still need to be further increased by unremittingly improving their electrical conductivity, specific surface area and ion diffusion rate.

Recently, nitrogen doped mesoporous carbon (NMC) has been widely recognized as one promising electrode material due to its satisfactory characteristics including fast electron transfer and electrolyte ions diffusion rate, high surface area, unique mesoporous structure, rich pore volume and excellent hydrophilic feature, which mainly arises from the introduction of nitrogen-containing groups [18–24]. In particular, Lu et al. reported novel nitrogen-containing ultramicroporous carbon nanospheres, which displayed a high specific capacitance of 269 F g^{-1} at 1.0 A g^{-1} and remarkable cycling stability [23]. Furthermore, nitrogen-containing carbon microspheres with a high nitrogen content of 5.94 at.% were produced via a convenient carbonization method, which achieved an excellent specific capacitance of 228 F g^{-1} at a current density of 1.0 A g^{-1} [24]. Although these great progresses have been made on the pristine NMC, no effort has been devoted to the design of electro-active NMC/NiCo-LDHs composites for supercapacitors. In this paper, novel microsphere-like nitrogen-doped mesoporous carbon/nickel-cobalt layered double hydroxide (NMC/NiCo-LDHs-M) was firstly developed via an efficient microwave method and used as novel electrode materials for EPCs in the hope of achieving a sufficient and fast redox reaction, which can ensure a high specific capacitance and long cycle life. As expected, the application of microwave method is very helpful in preparing high performance electrode materials for supercapacitors because it possesses the advantages of high reaction rate, homogeneous heating rate and excellent energy-saving properties [25,26], which is highly superior to the conventional hydrothermal process.

2. Experimental

2.1. Reagents and materials

Triblock copolymer pluronic F127, dicyandiamide, urea, HCl, HF, ethanol, formaldehyde, NaOH, phenol, $Ni(NO_3)_2\cdot 6H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ were supplied by Sigma-Aldrich Co. Ltd (USA). Silica (HL-380) template was purchased from Guangzhou GBS High-Tech & Industry Co. Ltd (China). All reagents in our experiments were of analytical grade and used as received.

2.2. Synthesis of NMC

2.2.1. Synthesis of phenolic resin

Just as described in literature [27], 8.0 g phenol was mixed with 1.7 g NaOH solution (20 wt%) under continuously stirring at 70 °C, followed by adding 14.2 g formaldehyde solution (37 wt%). After naturally cooling down to room temperature, pH value of the above mixture was adjusted to about 7.0 using 2.0 M HCl solution. Subsequently, the as-prepared substance was dried in a vacuum oven at 45 °C and the final product was dissolved in ethanol to obtain a phenolic resin solution with a concentration of 20 wt%.

2.2.2. Preparation of silica colloid

Briefly, 0.478 g commercial silica (HL-380) was dispersed in 100 mL ethanol and sonicated for 1 h to form a homogeneous dispersion.

2.2.3. Synthesis of NMC

NMC was synthesized using a dual-template method with a small modification [28]. The above synthesized phenolic resin was used as a carbon source, dicyandiamide as a nitrogen source, commercial silica (HL-380) as a hard template and triblock copolymer pluronic (F127) as a soft template respectively. In a typical preparation process, 1.6 g F127 was dispersed into 10 mL ethanol in advance and then was dropwise added into the as-prepared silica colloid. After that, 5 g phenolic resin solution (20 wt%) and 0.05 g dicyandiamide were added into the above solution drop by drop under continuous sonication. Afterwards, the mixture was transferred to a surface dish to volatilize ethanol at room temperature and then dried at 100 °C for 24 h. After the obtained composites were respectively maintained at 200, 350 and 500 °C in N_2 atmosphere for 2 h, it was heated to 700 °C with a heating rate of 2 °C min^{-1} and kept for 2 h. Finally, the resulted silica/carbon composite was treated with HF solution (15 wt%) for 48 h to remove silica, washed with deionized water and dried at 60 °C for 24 h to obtain NMC.

2.3. Synthesis of NMC/NiCo-LDHs-M by microwave method

The NMC/NiCo-LDHs-M nanocomposites were synthesized via a microwave method using urea as alkali source. Briefly, 0.0085 g NMC was dispersed in 60 mL ethanol aqueous solvent (50 wt%) to form a homogeneous dispersion under sonication. Then, 0.566 g $Ni(NO_3)_2\cdot 6H_2O$, 0.291 g $Co(NO_3)_2\cdot 6H_2O$ and 0.96 g urea were further added, respectively. Subsequently, the above dispersion was transferred to a Milestone Microsynth Microwave oven (Germany) and treated at 120 °C for 30 min. Finally, the obtained black products were centrifuged, washed with deionized water and vacuum-dried at 60 °C for 24 h.

In the case of clarifying the role of microwave heating on the structural and electrochemical performance of NMC/NiCo-LDHs, microwave method and conventional hydrothermal process were employed under the same reaction conditions, and their products were named as NMC/NiCo-LDHs-M and NMC/NiCo-LDHs-H, respectively. In addition, pristine nickel-cobalt layered double hydroxide (NiCo-LDHs-M) was synthesized according to the same microwave procedures without adding NMC.

2.4. Characterization

Elemental analysis of the C and H was carried out with the Elemental Analyzer (Perkin-Elmer 2400 Series II CHNS/O). The actual content of nickel and cobalt were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Powder X-ray diffraction (XRD) patterns of the products were collected on a

Table 1
Element analysis results of the NMC/NiCo-LDHs-M that was prepared by microwave method.

Sample	Ni (%)	Co (%)	C (%)	N (%)	H (%)	O (%)
NMC/NiCo-LDHs-M	38.17	18.80	2.44	4.63	2.11	33.85